DARPA R&D Status Report

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Contract Amount: \$2,582,405

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Effective Date of Contract: June 26, 1996

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Short Title of Work: Non-toxic, Self-cleaning Silicone Fouling Release Coatings

Reporting Period: April through June, 1997

Description of Progress:

Task 1: Design, synthesis and testing of foul-release paints with improved antifouling and release properties

Task 1.1: Design, synthesis and testing of foul-release paints (GE-CRD) Because Duplex coatings containing silicone oils encapsulated with hard Thermoset wall materials exhibit poor abrasion resistance and a high degree of fouling, two microcapsule manufacturers have been identified for preparation of gel wall microencapsulations.

A carbinol terminated PDMS and two ablative oils were synthesized for use in the compositions downselected for panel preparation for subcontractor sites. Twelve panels of each of twelve downselected formulations and a control were prepared, by either spray application or by drawdowns depending on material availability, and distributed to SUNY-Buffalo, Bridger Scientific, FIT, and Hawaii. An additional 9 panels were prepared for Bridger Scientific deployment at a site in Massachusetts. Panels were also prepared for deployment at FIT. These include a tethered oil and a tetherable antimicrobial.

Task 1.1.1: Quantitative foul-release performance of new materials (FIT) Two instrumented foils, that can measure the skin friction drag forces on 10" x 12" panels, are now in operation and calibration trials using known surfaces and shapes are being completed. An initial set of panels, including GE0, J501, Ablative Copper and Epoxy, are being run and will be exposed to biofouling to ascertain skin friction and foul release properties.

A total of 78 test panels were exposed to barnacle fouling at the Florida Institute of Technology static immersion site in January 1997 and a further 45 panels immersed in April 1997. These were caged to

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prevent loss of barnacles by fish predation. Barnacle adhesion measurements were made on all the January panels and some of the April panels.

Task 1.1.2: Field Exposure Testing (Bridger Scientific)

Preliminary exposure panels, representing four coating formulations, have been immersed at two designated utility sites (Somerset, MA and Providence, RI) for approximately four months. Test and control panels at both locations have been inspected three times (March, April, June); all have been evaluated for foul resistance (ASTM D3623), and for foul release/adhesion properties, where possible (water jet, ASTM D5618).

At Somerset, MA, spatial differences in the pattern, density and adhesion of fouling with position on the rack assembly (top/bottom) continue to persist. Two panels from each group were selected and their positions were interchanged. At the time of the last inspection (6/6/97), no hard fouling was observed on any of the foul release coatings; attached hydroids were present only on the RTV11 and RTV11 + 10%SF1154 materials. Barnacles (5 - 10 mm) were attached to the uncoated controls and rack frames.

The rate and extent of fouling at Providence, RI are significantly greater than that observed at Somerset, MA. Control (uncoated) panels were covered 20 - 40% with adult (8 - 13 mm) barnacles; hydroids and blue mussels (10mm) were also present but to a lesser extent. Attached sediment/slime on the foul release materials was more dense. Barnacles were present on the RTV11 and RTV11 + 10%SF1154 materials; no other attached hard fouling species were observed. Barnacle adhesion strengths were measured (when present).

Task 1.2: Validation Testing (NSWC)

Steel panels were blasted and shipped to GE CRD for the first round of marine panel exposure tests. Control copper panels were shipped to exposure sites.

Task 2: Optimize Coating Physical and Application Properties

Task 2.1 Physical Property Optimization (GE-CRD)

A total of 110 panels were evaluated for abrasion resistance, qualitative adhesion and HATE adhesion. Compositions which provided low barnacle adhesion values, good qualitative adhesion and abrasion resistance were identified.

Twelve compositions were downselected on May 15-16 in Ft. Lauderdale, Florida for entry into phase 2, based on physical property measurements performed at CRD, barnacle adhesion data obtained form FIT and fouling data from Miami Marine Research and Testing Station.

Die-B Tear values were obtained for several oil containing compositions. Oil incorporation did not significantly alter the Die B tear strength.

Task 2.1.1 Cleanability of foul-release coatings (SUNY)

Coatings for the next phase of field trials, selected at the May 15/16 program meeting in Florida, were prepared by GE-CRD and received by the University at Buffalo team on 30Jun97. The coated panels will be logged in and prepared for field exposure at UB's two fresh water sites in Western New York, to be immersed in mid-July. Prior to immersion, one panel of each coating type will have a narrow coated band cut from one end, for pre-exposure surface analyses. The cut edge of each panel sampled in this way will be sealed with Wacker J501 [black] before the panel is deployed. Several similar panels, currently immersed at the test sites, had been cut and sealed in this manner without any untoward effects.

Infrared spectroscopic analysis of oils used in some of the downselect coatings was completed; data will be used for calibration and interpretation of IR spectra of coating surface zones and transferred residues.

All racks and test panels at the Dunkirk site, removed from the water on 29Jan97 due to an ice jam, were stored safely indoors until 09Apr97, when they were returned to the Lake Erie water. Prior to reimmersion, waterline panels were added to the racks; this completed an action item from the mid-January program meeting at NSWC. The first observations of fouling on the panels will take place in mid-July.

Field notes, taken over the past 5 years, were reviewed for observations of the frequency and severity of grazing by fish, snails, and other species from fouling-release coatings immersed at the two sites. Both frequency and severity were low. In April, coated concrete panels, immersed at the Medina site for nearly a year and arranged to prohibit grazing on half of the surfaces, were inspected. The extent and type of fouling present on protected versus unprotected areas were not different. It was determined that panel caging will not be necessary at the two test sites.

Four (4) steel control BRA640 panels were received from NSWC. Two of the panels will be immersed at the Dunkirk site and two at the Medina site, in mid-July. No pre-exposure analyses of these panels are planned; data obtained in the past for BRA640 in a Navy-sponsored program will be consulted.

Task 2.2: Field Demonstrations (NSWC)

A request was processed for patch testing of 3 GE promising candidates.

Task 2.3: Coating Application Development (GE)

Task 3: Environmental Impact and Toxicological Testing

Task 3.1: Environmental Impact (CRD)

Metal strips coated with crosslinked RTV and ¹⁴C labeled PDMS have been aging in both fresh water and salt water tanks for nearly three months. After two months in both fresh water and salt water, less than 0.08% of the total ¹⁴C was detected in the aqueous phase, and less than 0.03% of the total ¹⁴C was detected in the sediment. There was no measurable weight loss in any of the strips up to the two month time point. The data suggest that PDMS leaches extremely slowly from the crosslinked RTV.

A ¹⁴C-labeled poly(dimethyldiphenyl)siloxane (SF1154) has been coated onto metal strips with crosslinked RTV, and the strips have been suspended in both fresh water and salt water fish tanks for nearly two months. After one month in both fresh water and salt water, approximately 0.1% of the total ¹⁴C was detected in the aqueous phase, and less than 0.05% was detected in the sediment. The data suggest a faster rate of depletion of SF1154 as compared to PDMS, but the rate of depletion is still very slow. Again, no measurable weight loss was observed in metal strips removed from each tank at the one month time point.

Task 3.2: Toxicological Studies (NCCOSC)

A work request was issued by NSWC to NCCOSC for toxicity testing. Toxicology samples made by GE CRD using (a) formulations of RTV11 + 10% oil additives and (b) a proprietary formulation were sent to NCCOSC for testing.

Change in Key Personnel:

None.

Summary of Substantive Information Derived from Special Events:

A DARPA team meeting was held May 15-16, 1997, at the Navy testing station in Ft. Lauderdale, FL. The GE physical property test data, Bridger Scientific field exposure fouling test data, and FIT barnacle adhesion test results were presented and a preliminary downselect list determined. A visit to Miami Marine Research and Testing Station and a review of the selected formulations yielded a final first downselect list of 12 compositions.

Problems Encountered and/or Anticipated:

None

Action Required by the Government:

None

Fiscal Status:

(1) **Project Cost:** \$ 952,633 (2) **Cost Share:** (230,395) (3) **Net to ONR/DARPA:** \$ 722,238